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MOCVD Synthesis of Group III-Nitride Heterostructure Nanowires for Solid-State Lighting

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Abstract

Solid-state lighting (SSL) technologies, based on semiconductor light emitting devices, have the potential to reduce worldwide electricity consumption by more than 10%, which could significantly reduce U.S. dependence on imported energy and improve energy security. The III-nitride (AlGaInN) materials system forms the foundation for white SSL and could cover a wide spectral range from the deep UV to the infrared. For this LDRD program, we have investigated the synthesis of single-crystalline III-nitride nanowires and heterostructure nanowires, which may possess unique optoelectronic properties. These novel structures could ultimately lead to the development of novel and highly efficient SSL nanodevice applications. GaN and III-nitride core-shell heterostructure nanowires were successfully synthesized by metal organic chemical vapor deposition (MOCVD) on two-inch wafer substrates. The effect of process conditions on nanowire growth was investigated, and characterization of the structural, optical, and electrical properties of the nanowires was also performed.

Acknowledgments

We would like to acknowledge the technical contributions of Donald J. Werder and Paula P. Provencio with regards to the TEM characterization of the nanowires, of Elaine Lai with regards to the electrical measurements of the nanowires, and of Richard J. Anderson, Steven R. Kurtz, and Tom Bauer with regards to assistance with the optical characterization of the nanowires. We also acknowledge helpful discussions with Daniel D. Koleske.

Table of Contents

List of Figures

1. Introduction

The purpose of this LDRD project is to develop scalable based processes to synthesize and characterize single-crystalline III-nitride nanowires and heterostructure nanowires for potential novel solid-state lighting (SSL) and photonic nanodevice applications. SSL technologies, based on semiconductor light emitting devices, have the potential to reduce worldwide electricity consumption by more than 10%, which could significantly reduce U.S. dependence on imported energy and improve energy security. The III-nitride (AlGaInN) materials system forms the foundation for white SSL and could cover a wide spectral range from the deep UV to the infrared. Single-crystalline III-nitride nanowires and heterostructure nanowires may possess unique optoelectronic properties due to their structural quality, size and dimensionality. This could ultimately lead to the development of novel and highly efficient SSL devices based on III-nitride nanowires.

Our approach focuses on using metal-organic chemical vapor deposition (MOCVD) to synthesize the nanowires on 2-inch wafer substrates in a conventional cold-walled rotating disk reactor. MOCVD is a versatile, reproducible technique with excellent control that is in widespread commercial use for the growth of compound semiconductor devices, including light emitting diodes (LEDs) and solid-state lasers. We believe that success in developing MOCVD-based techniques for synthesizing III-nitride nanowires with controlled orientation and properties would represent a major advance in nanowire device research, and hence nanowire-based lighting, by allowing for the scalable and reproducible growth of heterostructure nanowires (e.g. quantum well nanowires), tunable band gap AlGaInN alloy nanowires, and n-type and p-type doped intra-nanowire junctions. Additionally, MOCVD-based nanowire growth would allow for facilitated scalability and integration with film technology, as well as a direct technology transfer to a large installed base of MOCVD reactors, using standard precursors for growth and doping. Thus, MOCVD arguably represents the most promising method for the controlled growth of III-nitride nanowires for nanodevice applications. The nanowires were grown using metal catalyst nanoclusters deposited on the substrate surface to initiate and direct nanowire growth via the vapor-liquid-solid mechanism.[1]

This LDRD was funded over the fiscal period FY04-FY06, for $100K per year, under LDRD project number 79800, under the Investment Area/Thrust of Energy and Infrastructure Assurance/Innovating in Energy and Infrastructure Assurance.

2. Experimental Details

The growth experiments were performed in a home-built MOCVD rotating-disk cold-wall reactor, which is shown in Figure 1. The substrate holder temperature was measured and controlled using a commercial near-infrared pyrometer. Two-inch diameter sapphire or silicon wafers were used as the growth substrates. Nickel served as the catalyst for vapor-liquid-solid (VLS) based nanowire growth and was deposited on the substrate surface prior to insertion into the reactor. The nickel was typically deposited as either a thin nickel film (2-5 nm thick) or in the form of NiO nanoparticles (8-10 nm diameter) or nickel nitrate (hexahydrate) ($Ni(NO_3)_2$-$6H_2O$) dissolved in absolute ethanol to the desired concentration and subsequently sonicated and applied drop-wise via a pipet onto different areas of the substrate. Following application of the catalyst, the wafer was placed into the reactor for growth. After heating to the desired growth temperature in hydrogen (H_2), trimethylgallium and ammonia (NH_3) were introduced into the reactor to initiate nanowire growth. The reactor pressure was held constant at 140 Torr and the wafer rotation rate was 1200 RPM.

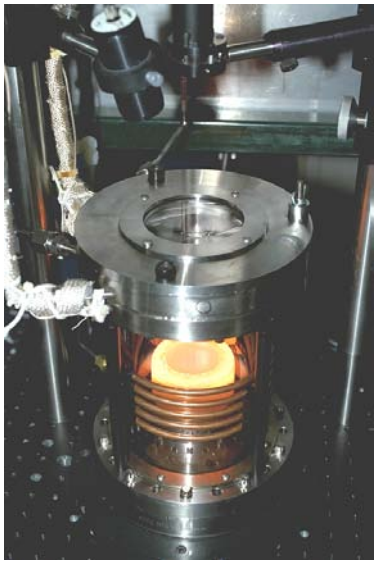

Figure 1. Cold-wall rotating disk MOCVD reactor used for nanowire growth

The nanowire growth was characterized with scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Electrical characterization of individual nanowires was carried out by first sonicating nanowires in 2-propanol, followed by spin-casting the suspension onto p+ Si wafers with 100 nm thick thermal oxide. Next, arrays of interdigitated Ni/Au (40nm/70nm) electrodes were defined on the substrate using optical lithography, followed by an O_2 plasma descum etch and electron beam evaporation and lift-off. Each interdigitated electrode array contains 32 individually addressable electrodes, as shown in Figure 2, with a spacing of 1 μm, 2 μm, or 4 μm. This approach does not require direct write electron beam lithography, and generally results in tens to hundreds of individual nanowire devices. Before testing, the wafers were annealed for several minutes at 600 °C in vacuum, which resulted in formation of ohmic contacts to the nanowires. Photoluminescence (PL) spectra were collected on individual nanowires using a home-built system, in which light from a 325 nm He-Cd laser is focused through a reflective UV lens into a 10 μm spot, with a total incident power of 2 mW.

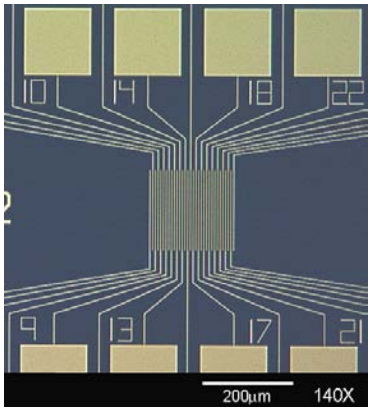

Figure 2. Optical image of interdigitated electrode array used for nanowire electrical measurements

3. Results

3.1 Nanowire Growth and Structural Characterization

We have demonstrated the growth of single crystalline GaN nanowires using MOCVD on two-inch sapphire and silicon wafer substrates. Figure 3 shows the growth of GaN nanowires on *c*-plane (0001) sapphire at 800 °C. While densely packed, the nanowires are not seen to have a high degree of alignment with respect to the substrate. Control of both the growth orientation, which can have a strong effect on anisotropic properties, and alignment are critical issues in nanowire growth. In particular, the ability to control the nanowire alignment could enable devices based on arrays of vertically aligned III-nitride nanowires and heterostructure nanowires. Thus, we explored the effects of substrate orientation of nanowire alignment. In a breakthrough, we were able to achieve the growth of highly aligned, uniform arrays of vertically aligned GaN nanowires on (1-102) *r*-plane sapphire substrates under certain conditions, as shown in Figure 4. Significantly, the nanowires were grown without the use of a template or patterning.

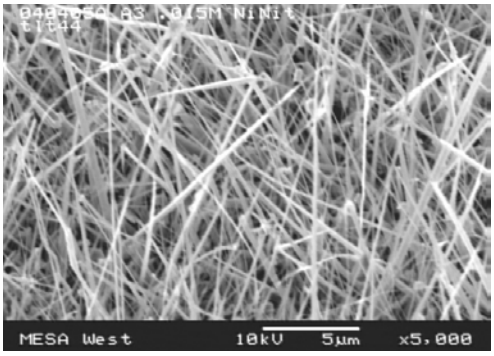

Figure 3. SEM image of GaN nanowires grown by MOCVD at 800 °C on c-plane (0001) sapphire

Interestingly, we found that the degree of alignment and size uniformity of the nanowires were dependent on the nickel nitrate catalyst concentration applied to the substrate, with the highest degree of uniformity and alignment occurring at concentrations much more dilute than typically employed for VLS-based nanowire growth. Specifically, regions of highly aligned growth were most often observed at nickel nitrate concentration of 0.0005 M, as shown in Figure 4. This concentration is approximately 20 times or more dilute than typically used for the growth of carbon nanotubes and semiconductor nanowires[2-5], and to our knowledge the use of such dilute concentrations and the results on VLS nanowire growth have not been previously reported. In these highly aligned regions, the GaN nanowires had typical diameters at their base of ~200-400 nm and very small diameter tips with an average diameter of 10 nm ± 8 nm, with the majority having tip diameters below 9 nm. The majority of the nanowires had lengths of ~5-10 μm, and the density of the nanowires was approximately 3.5 μm^{-2} in the highly aligned 0.0005 M nickel nitrate areas. The GaN nanowires typically have a tapered, or needle-like, shape, and triangular cross-sections, as was also seen in previous studies of MOCVD-grown GaN nanowires.[4,6-8] The tapered shape is most likely due in large part to competing homoepitaxial growth on the nanowire sidewalls. Near top-view SEM images (e.g., Figure 4) show that the vertically aligned nanowires have their respective facets aligned in the same directions, indicating a common growth orientation.

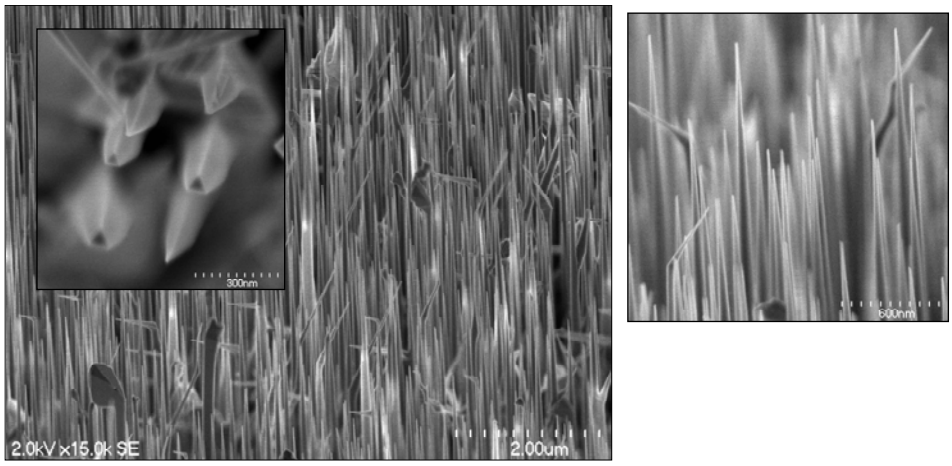

Figure 4. SEM images of highly aligned growth of GaN nanowires at 800 °C on *r*-plane (1-102) sapphire

The structural characteristics of the aligned nanowires were investigated by transmission electron microscopy (TEM), which showed that the GaN nanowires have a single crystalline, wurtzite structure. Figure 5 shows a high resolution TEM image and corresponding selected area electron diffraction (SAED) pattern an individual GaN nanowires, with the [0001] zone axis parallel with the electron beam direction. From the alignment of the real space image and the diffraction pattern, the nanowires were determined to grow along the [11-20] direction, perpendicular to the (11-20) *a*-plane of GaN. A small proportion (<15%) of the nanowires were determined to have a [10-10] growth direction. The triangular sides of the [11-20] oriented nanowires were determined to consist of the (0001), (-1101), and (-110-1) planes, resulting in an isosceles cross-section. Significantly, no threading dislocations were observed in the nanowires, although (0001) basal-plane stacking faults were commonly observed. (0001) stacking faults are known to have a low defect energy and are frequently observed in GaN films[9-13] and have also been reported in GaN nanowires.[14-17]

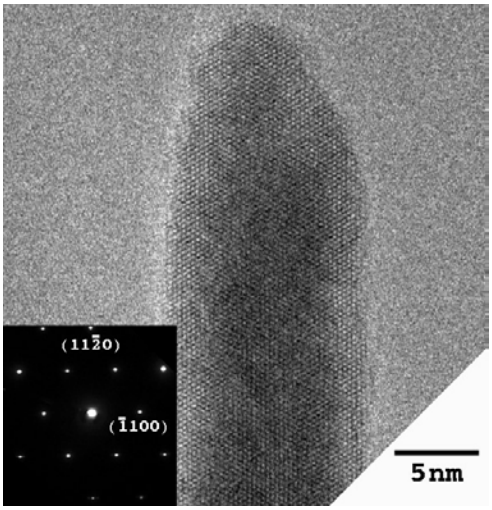

Figure 5. HR-TEM image of [11-20] oriented GaN nanowire

Using our experience in the growth of GaN nanowires via MOCVD, we have also been able to create radial, or core-shell, heterostructure nanowires. The GaN nanowires serve as the "core" upon which shell layers of different III-nitride materials can be heteroepitaxially deposited. We have been able to achieve this by varying the process conditions such that axial nanowire growth is quenched and the new layer grows radially to form a shell around the GaN nanowire core. In this manner, we have synthesized core-shell nanowires with GaN cores and AlN, AlGaN, InN, and InGaN shell layers, on 2-inch sapphire substrates. An example of an GaN-InN core-shell nanowire grown using this technique is shown in Figure 6. We have found that accurate structural and compositional characterization of the heterostructures nanowires has proven non-trivial. Perhaps due to the triangular faceting, standard bright-field TEM imaging does not reveal the distinct inner core and outer shell layer, making a determination of shell thickness and uniformity difficult.

3.2 Optical and Electrical Characterization of Nanowires

We collected photoluminescence (PL) measurements of individual GaN nanowires at room temperature to gauge their optical quality. Representative PL spectra for nanowires grown at 800 °C are shown in Figure 6a. A band-edge emission peak at around 368 nm and a broad yellow luminescence band centered around 550 nm. The band-edge peak is slightly red-shifted compared to a 363 nm band-edge peak measured under the same conditions for a

commercially obtained *c*-plane GaN film (TDI, n-type undoped). The yellow luminescence band is commonly observed in undoped GaN films, and despite intense investigation, it is still unresolved as to its exact source.[18] However, several studies have linked the yellow luminescence to the presence of carbon[19-24], which is thought to act as an acceptor-type electron trapping center in GaN.[25,26] We note here that GaN is typically grown by MOCVD at temperatures exceeding 1000 °C, and that increasing carbon incorporation in MOCVD-grown GaN has been correlated with decreasing growth temperature.[27] In order to determine whether increasing the growth temperature of the nanowires would increase the ratio of the band-edge peak height to the yellow band height (BEL/YL), GaN nanowires were grown at an increased temperature of 900 °C on *r*-plane sapphire, keeping all other growth conditions the same. Representative room temperature PL spectra of the nanowires grown at 900° C are shown in Figure 6b, and show a dramatic increase in the BEL/YL ratio, indicating the nanowires have excellent optical and crystalline quality, even in the absence of intentional doping. Specifically, we observe a ~50 times increase in the absolute band edge peak intensity and an approximate two orders of magnitude increase in the BEL/YL ratio compared to the nanowires grown at 800 °C (shown in Figure 6a). Thus, our results show that the optical quality of MOCVD-grown GaN nanowires is highly dependent on growth temperature, which is most likely due to increased carbon incorporation from the trimethylgallium precursor at lower growth temperatures.

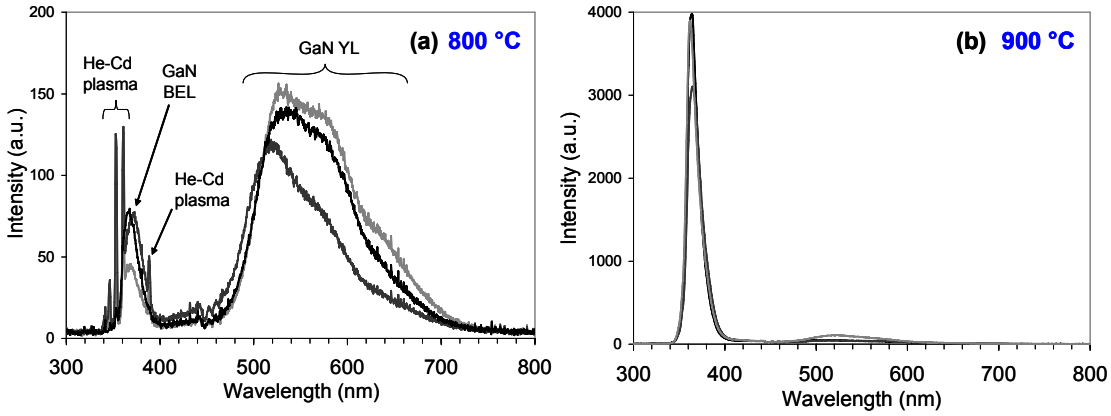

Figure 6. Representative PL spectra of GaN nanowires grown at (a) 800 °C and (b) 900 °

Electrical measurements were also performed on the aligned GaN nanowires grown at 800 °C and 900 °C, and are shown in Figure 7. The electrical properties, similar to the optical properties, were seen to be highly dependent on growth temperature, with a typical resistivity of ~1 Ω·cm for nanowires grown at 900 °C and ~1000 Ω·cm for 800 °C grown nanowires was measured. We have observed a sharp increase in resistance for GaN nanowires with smaller diameters (< ~200 nm), irrespective of growth temperature and presumably due to depletion by surface states.[28] It has been suggested in numerous studies that carbon substituting on nitrogen sites, acts as a deep acceptor in GaN[22], and increasing resistivity in GaN films with increasing carbon concentration has been previously reported.[29] Thus, increased incorporation of carbon from the trimethylgallium source at lower growth temperature[27] could lead to compensation of the free carriers in GaN. This explanation is also in agreement with the sharp decrease in the BEL/YL ratio for the 800 °C vs. 900 °C grown nanowires reported here.

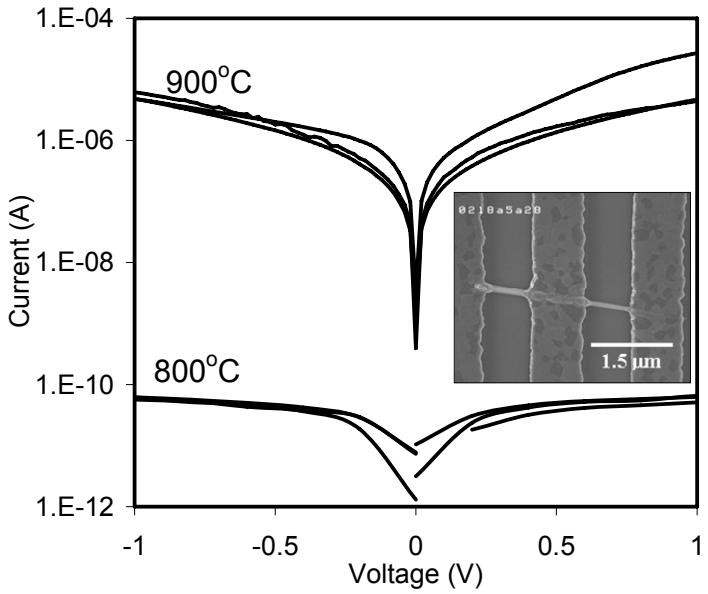

Figure 7. Representative I-V data for GaN nanowires grown at 800 °C and 900 °C. Inset shows a single GaN nanowire device with top-deposited contacts.

Preliminary studies of the optical properties of core-shell heterostructure nanowires were also carried out. Figure 8 shows photoluminescence spectra for GaN-InGaN core-shell nanowires grown at 900 °C and 750 °C for the core and shell, respectively. In comparison, to GaN nanowires, the PL spectra of GaN-InGaN heterostructure nanowires show new peaks at ~400-410 nm, as seen in Figure 8, indicating emission from the InGaN shell layer. By altering the growth conditions, and hence the degree of In content, it will be possible to tune the emission wavelength of the InGaN shell layer into the blue and green region of the visible spectrum. While the InGaN emission in these nanowires is not particularly intense compared to the yellow band emission, it demonstrates a proof of concept for core-shell nanowires as potential solid-state lighting components. Future work will focus on improving the band-edge emission of the InGaN layers and tuning the emission wavelength.

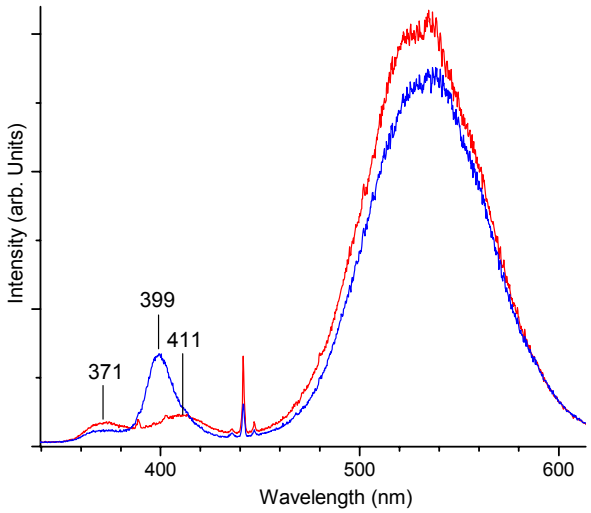

Figure 8. PL spectra of GaN-InGaN core shell nanowires showing InGaN peaks

4. Conclusions

For this LDRD project, we have investigated techniques based on MOCVD to synthesize GaN and III-nitride heterostructure nanowires for potential use as elements in future solid-state lighting devices. We were successfully able to synthesize high quality, single-crystalline GaN nanowires using MOCVD on standard sapphire substrates. By careful

selection of the substrate orientation and catalyst preparation, we were also able to achieve the highly aligned growth of vertical nanowire arrays without the use of patterning, which could lead to devices based on dense arrays of oriented nanowires. The optical and electrical properties of single nanowires were measured using a Sandia-developed platform. Building off our GaN nanowire growth expertise, we were also able to fabricate core-shell III-nitride heterostructure nanowires with GaN cores and shells of various composition, including InN, InGaN, AlGaN, and AlN. Structural characterization to determine shell layer thicknesses and quality were found to be non-trivial on these core-shell nanowires, perhaps due to their triangular cross-sections. Preliminary optical characterization of GaN-InGaN core-shell nanowires did indicate emission from the InGaN layer, demonstrating that these core-shell nanowires could be promising candidates as efficient elements in future solid-state lighting devices.

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